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PHOSPHATES IN ORNITHOGENIC SOILS OF THE MARITIME ANTARCTIC

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Abstract: Ornithogenic soils have been formed in stony loams on and around penguin rookeries along the sea shore of the maritime Antarctic. The fine fraction of these soils contains mainly posphates of various chemical and mineral compositions. Genetic horizons of ornithogenic soils resulted from diversified mineral composition of them in the vertical profile. Occurrence of apatite, brushite, struvite, urates(?) fluorite in the surface guano layer, and leucophosphite, minyulite, taranakite, vivianite, amorphous and crystalline phosphates in the phosphatized rock zone was documented. Among crystalline aluminium phosphates besides vashegyite, a new mineral arctowskite was distinguished. Chemical composition, X-ray pattern, microscopic images of all selected phosphates was given. Most of the phosphates are relatively long-lasting under climatic conditions of the maritime Antarctic, and can be found in the places abandoned by penguins hundreds and thousands of years ago. A high content of nutrients is available for the poor tundra vegetation growing around current and over the relic ornithogenic soils, and can be an important factor controlling their productivity, chemical composition and probably also species diversity.

1. Introduction

During the nesting period penguins gather on the ice-free strips of land in the maritime Antarctic Zone. Biogeochemical cycle of nutrients on the land/sea interface resulted from bird activity has been studied by a Polish scientific team for ten years, and described in a series of papers. Heavy manuring of the rookery area by krill-eating penguins results in the formation of phosphatic soils on and around breeding sites (TATUR and MYRCHA, 1984; TATUR, 1989). These soils are long-lasting under climatic conditions of the maritime Antarctic and thus also occur on the areas abandoned by penguins long time ago (TATUR and DEL VALLE, 1986; TATUR and MYRCHA, 1989). Studies on soil-forming processes have also included excreta and guano decomposition (PIETR *et al.*, 1983; PIETR, 1986), changes in chemical composition of guano solution running off from the rookery and percolating throughout the soil (TATUR and MYRCHA, 1983), and mineral composition of recent and relic ornithogenic soils (TATUR and BARCZUK, 1984, 1985; TATUR, 1987, 1989). A general aspect of research was summarized in papers dealing with the effect of penguin colonization on the development of poor tundra ecosystems (MYRCHA *et al.*, 1985; MYRCHA and TATUR, 1988) and with

specific features of ornithogenic nutrient cycles in this region (TATUR and MYRCHA, 1990).

An earlier mineralogical description of phosphates forming ornithogenic soil is based on the study from King George Islands only. New data on minerals presented in this paper come from the material collected from the whole region of the maritime Antarctic, including relic soils of ornithogenic origin. Detailed description of the soil profiles is given elsewhere (TATUR, 1989).

2. Methods

Chemical analyses of the phosphates were carried out using AAS (Ca, Mg, K, Na, Al, Fe, Mn, Sr, Zn, Cu), colorimetric method (P) and elemental analysis (CHN). Data on X-ray diffraction and infra-red spectroscopy were collected. Studies in petrographic and scanning electron microscope and energy dispersive X-ray microanalyses have also been carried out. The scanning microscope micrographs were made by Andrzej ROCHEWICZ. A revised molecular formula of minerals was calculated on the basis of chemical analyses presented by TATUR (1989) and on the basis of new fluorine determinations made by KECK in selected samples using CULIK (1986) method, modified with direct potentiometry (F-ion selective combination electrode ORION 96-09), including standard addition technique.

3. Results

Ornithogenic soils consist of the surface guano layer and the underlaying phosphatized rock zone. In guano layer, besides organic matter, apatite commonly occur. Sometimes struvite, urates and probably traces of fluorite are present. In phosphatized rock zone the most popular are leucophosphite and amorphous aluminium phosphate. In a few places only taranakite, minyulite and vivianite can be found. In abandoned ornithogenic soils, minute amounts of crystalline aluminium phosphates can be sometimes formed.

Urates commonly occur in minor amounts as minute, white, agglomeration of nodules with spherulitic structure composed of pure minerals, usually between 2–20 μm in diameter (Fig. 1). They are dispersed on the surface of stones around penguin nesting places and can also be found as a minor component of fresh guano, but never occur in relic soils (TATUR, 1989). Chemical composition and X-ray data yield variable results but are indicative of urate salts of various degree of hydration. One average example is given below:

$$[(NH_4)_{0.69}K_{0.07}Na_{0.04}]_{0.80}(Mg_{0.06}Ca_{0.04}Fe_{0.03})_{0.10}C_5H_3O_3N_4$$

X-ray data: 3.22/100, 8.71/4, 5.64/4, 2.03/3.

Struvite occurs mainly as a superficial film on the guano layer adjacent to recent penguin rookeries. Sometimes it is also present as an important component of fresh guano. It forms sometimes, in paragenesis with apatite, a hard crust (usually a few mm thick) on the rocks and stones where guano solutions are running off from the rookery (Figs. 2 and 3). Struvite can also be found within the area of rookery, in precipitates

deposited at the margin of evaporating pools (TATUR, 1989). A pure and loose crystal agglomeration of the gravel fraction has been found in one place only, around the microsprings supplied with guano leachates (TATUR and BARCZUK, 1984). The chemical formula of struvite under study, $Mg(NH_4)PO_4*6H_2O$, usually contains a small excess of Mg over NH_4. The content of Mn, substituting Mg in formula of struvite, can be high (up to 0.51 percent) but only in the case when guano solutions percolated through the rock debris before crystallization of this mineral. A splendid X-ray pattern of this mineral is presented elsewhere (TATUR and BARCZUK, 1984, 1985).

Apatite is the main mineral of the guano layer in recent and relic ornithogenic soils. It forms a cryptocrystalline, earthy mass glued in nodular aggregates (Fig. 4), usually in a mixture with organic and mineral detritus (Fig. 5). The concentration of apatite in leached guano usually ranged between 30 and 60 percent (TATUR, 1989). It occurs also in association with struvite as a white lamina in a hard banded crust on the surface of the rocks and stones, and as a precipitate formed during evaporation of pools situated in the rookery area. However, a relatively pure agglomeration of this mineral can be found very rarely. Chemical analyses often reveal a small excess of Ca over P in the formula $Ca_5(PO_4)_3F$. The X-ray data are typical of apatite and usually rather clear in most of guano samples. The concentration of F is always very high and depends on Ca content. Thus the F/Ca ratio is relatively stable and similar to that in the theoretical formula of fluorapatite or sometimes even higher (TATUR, 1987). In samples with highest F concentration, the presence of fluorite traces was suggested from the X-ray data on the basis of the typical pattern.

In the one place only, in the guano deposit around cormorant nests (TATUR, 1989), concentration of F was found to be much lower (0.82 percent). F is capable to substitute in this case *co.* 36 percent of OH group in the formula of apatite. Thus the name hydroxyapatite seems to be more suitable for the apatite derived from cormorant guano. Results of infra-red analyses for both apatites did not contain CO_3^{--} spectra band, so the name apatite seems to be more precise to these guano minerals than francolite or other calcium phosphates usually common in such casses of occurrence (ALTSCHULER, 1973).

Concentration of trace elements is always very high in all guano samples rich in apatite. Sr up to 0.52%, Zn up to 0.16%, Cu up to 0.09% (TATUR, 1989). These trace elements originating from krill can substitute Ca in the molecular formula of apatite (ALTSCHULER, 1973).

In contrast to poorly crystalline apatite derived from guano, very well defined crystals of apatite (Figs. 6 and 7) were found in the fossil penguin bones, resting for about 40 Ma in the marine sediments (La Meseta Formation, Eocene/Oligocene, Seymour Island). The cross-section with the penguin bone bearing horizon has been presented elsewhere by MYRCHA and TATUR (1990). The molar ratio of Ca : P (5.9 : 3.0), and presence of CO_3^{--} band in the infra-red spectra suggest that this mineral is carbonate fluorapatite (francolite).

Brushite occurs in paragenesis with apatite in one place only, in a one-meter thick guano layer, near a current cormorant colony (TATUR, 1989). It forms well defined

monoclinic crystals, foliated, with perfect cleavage (Figs. 8 and 9) and with typical optical properties (NRIAGU, 1984). It was impossible to calculate the chemical formula of this mineral $CaHPO_4 * 2H_2O$ from the collected sample because of a high admixture of apatite. The X-ray data give an excellent pattern typical of this mineral:

7.53/100, 3.04/10, 4.23/9, 3.78/8, 2.62/6, 2.92/5, 2.00/3, 1.90/3, 2.80/1, 2.53/1.

However, intensity of reflections differs a little from the standard pattern presented by MURRAY and DIETRICH (1956).

Leucophosphite is the most common phosphate in the upper part of the phosphatized rock zone of recent and relic ornithogenic soils. It usually occurs as an important component of the clay mixture. However, it never forms monomineral agglomerations in the soil. Almost pure leucophosphite was recognized in one place only. It builds up subfossil penguin bones resting in well-aerated ornithogenic soils abandoned by penguins more than five thousand years ago (Fig. 10). Chemical analysis (outcrop 4bl in TATUR, 1989) suggests the following formula of subfossil bone leucophosphite:

$$[K_{0.31}(NH_4)_{1.69}]_{2.00}(Fe_{2.66\text{-}3.74}Al_{0.26\text{-}1.34})_4(PO_4)_4(F_{0.31}OH_{0.69})_2 * 4H_2O$$

X-ray pattern: 6.03/100, 3.07/91, 6.82/89, 2.85/80, 2.92/65, 3.02/57, 2.98/55, 2.67/50, 7.69/36, 4.79/36, 4.29/36, 2.73/34, 3.40/33, 1.93/33, 1.80/30.

The chemical analyses and X-ray data are comparable with the other natural and synthetic iron>aluminium leucophosphites bearing K and NH_4 ions (HASEMAN *et al.*, 1950; LINDBERG, 1957; AXELROD *et al.*, 1952; SIMMONS, 1964), including also the one separated by WILSON and BAIN (1976) from ornithogenic soil on adjacent Elephant Island. The shape of the crystals of leucophosphite has probably been destroyed by corrosion processes (Figs. 11 and 12).

Minyulite has been found in two profiles of ornithogenic soils situated in the vicinity of large recent penguin rookeries. Its occurrence seems to be typical of the upper and/or middle part of the phosphatized rock zone, where iron was entirely leached from the soil by strong action of guano solutions. The solutions supplied also high quantities of fluorine, necessary for the formation of this mineral (KAMPF, 1977). In one case, minyulite occurred together with leucophosphite as an important component of phosphatic clay (profile 4, 30–70c. cm in TATUR, 1989). In another case, it formed a hard porous layer of pure minyulite in the upper part of phosphatized rock zone, and contained grains of amorphous aluminium phosphate in the lower part (sample M in TATUR and BARCZUK, 1984; profile 5 in TATUR and MYRCHA, 1984; sample M in TATUR, 1987). In previous papers the following chemical formula of this mineral from the second locality was given: $K\,Al_2(F_{0.82}OH_{0.18})(PO_4)_2 * 4H_2O$, as well as an excellent X-ray pattern typical of this mineral.

However, new SEM images of minyulite forming the porous and hard layer (sample M) permitted a better recognition of its crystal habit. Micro-druses of slender prisms with orthorombic crystal system (KAMPF, 1977), but at the first view very close to tetrag-

onal one (Figs. 13, 14 and 15), covered as acicular radiating aggregates all the walls of a sponge-like structure. Slender prisms were up to 10 μm long and up to 1 μm wide in maximum dimensions. The shape of crystals was particularly well visible in one place with largest individuals (Figs. 16, 17 and 18), where in many crystals corrosion proceeding along Z axis weakness can be seen.

Taranakite sometimes abundantly occurs in the deepest horizons of ornithogenic soils in the area of recent and abandoned rookeries on King George Island (TATUR and BARCZUK, 1984; TATUR, 1989). Taranakite often forms a white, plastic and monomineral phosphatic clay composed of fine hexagonal plates, but after transport in water suspension, it also occurs as an earthy mass glued in aggregates. New analyses (TATUR, 1989) reveal that the simple chemical formula of this mineral presented in a former paper (TATUR and BARCZUK, 1984) is in fact a little more complicated:

$$[K_{1.4\text{-}1.9}(NH_4)_{1.1\text{-}1.6}]_3(Al_{4.4\text{-}5.0}Fe_{0\text{-}0.6})_5(PO_4)_8 * 18H_2O.$$

X-ray patterns of taranakite were always very clear and typical of this mineral.

Aluminium-iron phosphates. The recent study of ornithogenic soil (TATUR, 1989) delivered new information about this important group of minerals. The chemical composition of all of them is very similar, but X-ray diffraction data and the habit of crystals sometimes differentiate them very distinctly. Properties of phosphates described in ornithogenic soils of the maritime Antarctic are generally most similar to vashegyite mineral and amorphous aluminium phosphates described by KOCH and SARUDI (1964), MCCONNEL (1974), HSU (1982), and presented also by NRIAGU (1984). In one case, new unknown X-ray pattern and scanning microscope images were obtained, therefore arctowskite as a new mineral has been proposed for this occurrence. Vashegyite has been described in two slightly different examples of X-ray patterns, known from the literature (MCCONNELL, 1974; NRIAGU, 1984).

Amorphous aluminium-iron phosphate is common in both recent and relic ornithogenic soils. It occurs abundantly in the whole phosphatized rock zone and usually forms a glassy coat covering phosphatized grains of clastic material. Sometimes it contains a high amount of organic compounds. It can be concentrated at the bottom of ornithogenic soils, washed by melting waters, where it can form occasionally almost monomineral agglomerations with the following chemical composition: $Al_{10}(F_{2.5}OH_{0.5})_3(PO_5)_9 * 43H_2O$ (TATUR, 1987).

Amorphous aluminium phosphate, together with fluorapatite, also occurs in a white phosphatic crust mineralization covering the surface of stones exposed to guano solution running off from the rookery (Figs. 19 and 20). A new fluorine determination in one chosen crust sample (4.831 percent of F, sample-crust, C-I in TATUR, 1989), in which X-ray data gave only a weak apatite pattern, led to the following interpretation: besides *c.* 69% of fluorapatite, the phosphatic crust is formed in *c.* 25% by amorphous aluminium phosphate with the estimated formula: $Al_{10}F_9(PO_4)_7 * nH_2O$. This formula supports the observation of KAMPF (1977) about a strong affinity of Al^{3+} for F^- in the solution. A higher proportion of iron was noted in many crust samples, especially the ones coming from old mineralization. However, the Fe/Al molar ratio in such cases

did not exceed the value 0.5.

The concentration of trace elements (especially Sr) was very high in both examples of amorphous aluminium phosphates: Sr up to 0.55, Zn to 0.33, Cu to 0.02%. The enhanced content of these elements did not occur in the case of crystalline aluminium phosphates.

Crystalline aluminium phosphate (a new mineral, proposed name arctowskite in honor of a Polish scientist working in this part of Antarctica with Belgica Expedition 1897–1899). Arctowskite has been found in one place only. It occurs in the deepest horizon of the relic, ornithogenic soil at Low Head, King George Island, inside fissures of phosphatized boulders, surrounded by pure clay of taranakite (sample P-27, $<$50a cm, in TATUR, 1989). It forms white, plastic clay composed of well-defined rhombohedric crystals 2–5 μm in dimension, with angles 74° and 106°. Crystals are usually twinned in books (Figs. 21 and 22). They can be easily disintegrated into pieces (dehydration?) under the electron beam (Fig. 23). Energy dispersive X-ray microanalyses of several crystals clearly suggest a constant iron content in this mineral (Fig. 24). Total chemical analysis give the following formula: $(Al_{8.4}Fe_{0.6})_9(OH)_3(PO_4)_8 * \text{about } 27H_2O$. Concentrations of fluorine (0.105%) and sulphur ($<$0.01%) are negligible, the part insoluble in acids consists of *c.* 5% of the sample. X-ray analysis revealed a new pattern: 11.47/70, 11.21/100, 7.79/90, 7.56/70, 2.91/60. In the background a very weak X-ray pattern of taranakite occurs. Intensity of the other undefined reflections does not exceed 10%. Sample stored for six months in the ambient dry air of the laboratory has changed the X-ray pattern to: 9.37/40, 7.45/100, 6.81/10, 5.40/25, 2.90/60.

Many properties of arctowskite remind the ones of sasaite described by MARTINI (1978). The shape of crystals, mode of occurrence, as well as optical properties, are nearly the same. The X-ray pattern of fresh and dried sample and chemical composition also show many of similarities. Thus, in the original fresh sasaite the main reflections are 11.52/100, 7.51/22, 7.13/18, 6.99/23, 6.30/22, 4.214/18. Reflections 6.99, 6.30, 4.214, did not occur in arctowskite and the other ones are a little different. In original sasaite Al+Fe/P, molar ratio is *c.* 5% higher than in arctowskite. There is also a constant high sulphur concentration (2.77% of SO_4) included in the formula of sasaite. Sulphur did not occur in important quantity in arctowskite.

It should be noted, however, that sasaite, like arctowskite, is also very unstable in ambient dry air, and can easily change its structure due to dehydration. The product of this reaction seems to be comparable (on the basis of X-ray data) with the one obtained during dehydration of arctowskite. The X-ray pattern of sasaite dried in silica-gel are the following one: 9.33/100, 7.39/43, 6.47/22, 5.36/17, 3.091/18, 2.888/32, 2.859/27. The peaks with intensity above 15% were chosen from the data presented by MARTINI (1978). A better description of arctowskite and products of its dehydration would need much more detailed study on fresh and carefully stored material.

Crystalline aluminium phosphate, vashegyite-A, occurs in one place only, as a main component of a white clay covering a clastic material in the surface layer of relic ornithogenic soil (sample L-B in TATUR, 1989). It forms plates, not very well defined, usually rounded (Fig. 25). In the case presented on Fig. 26, the formation of vashe-

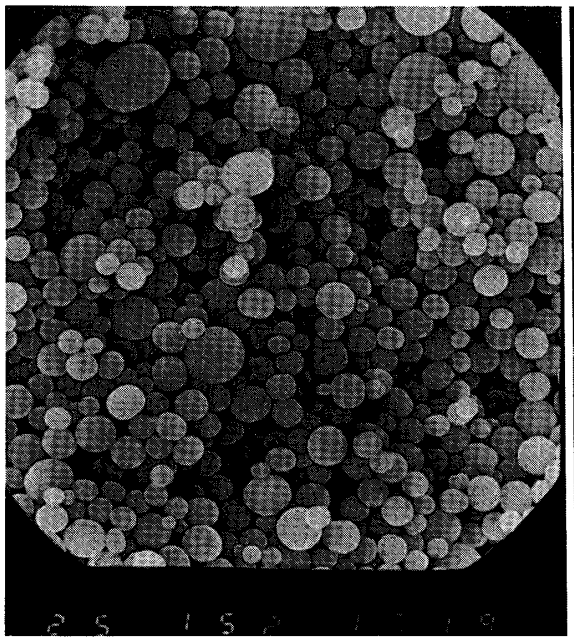

Fig. 1. Urates. Typical occurrence, spherules with fibrous structure.

Fig. 2. Struvite. Fracture of the crust. Dense lamination of struvite (dark) and fluorapatite (thin and light).

Fig. 3. Struvite. Druse on the surface of the crust (rare case).

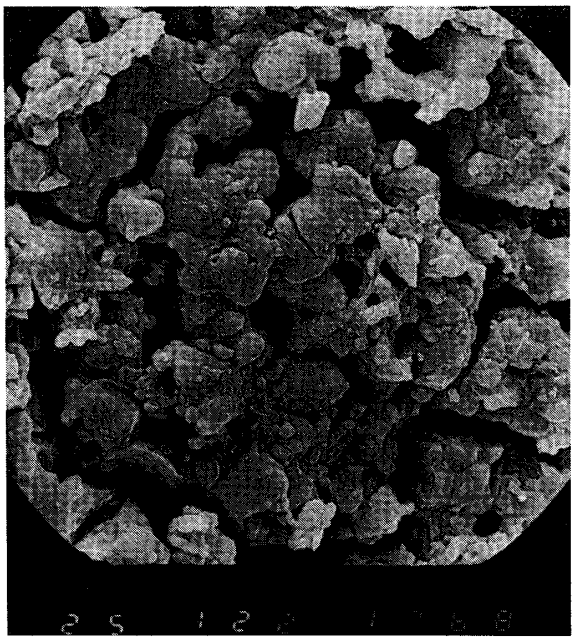

Fig. 4. Fluorapatite. Typical occurrence in guano. Earthy, nodular masses.

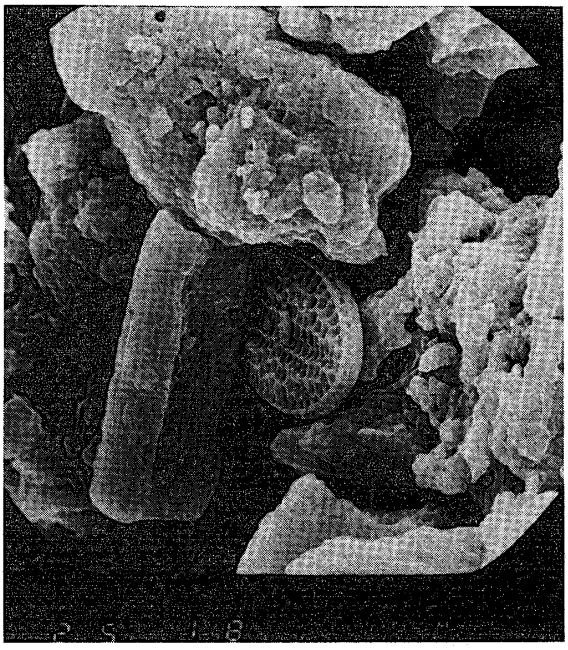

Fig. 5. Fluorapatite. Organic and mineral detritus among aggregates of fluorapatite from guano.

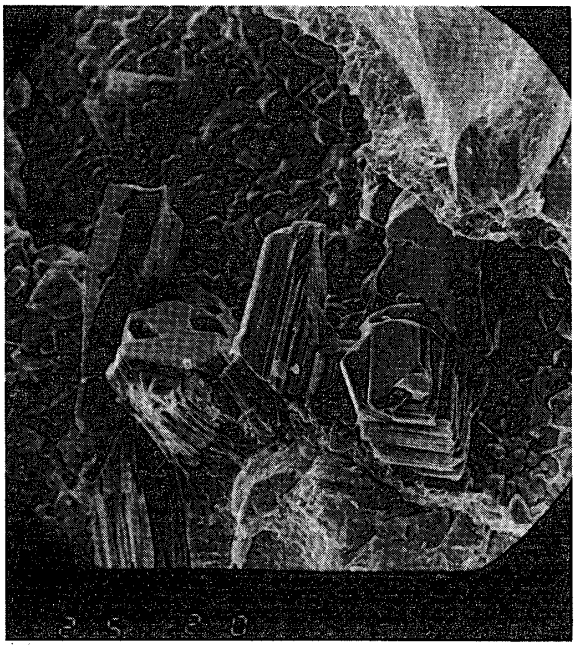

Fig. 6. (?) Carbonate fluorapatite. Fossil penguin bone. Prismatic and tabular crystals in druse.

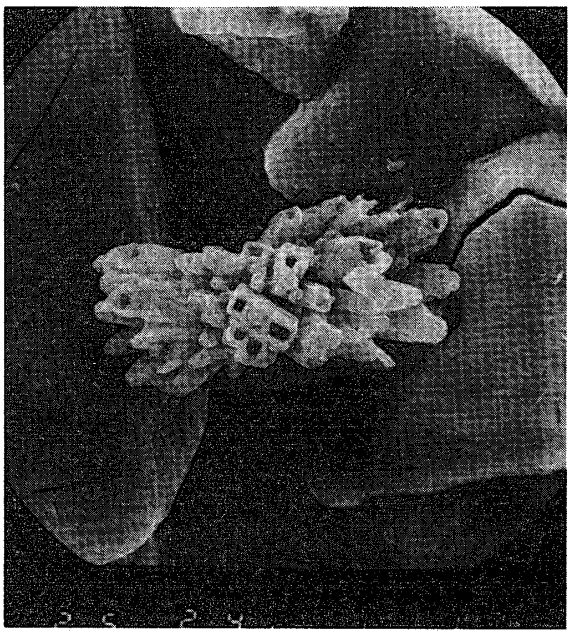

Fig. 7. (?) Carbonate fluorapatite. Fossil penguin bone. Recrystallization and corossion processes.

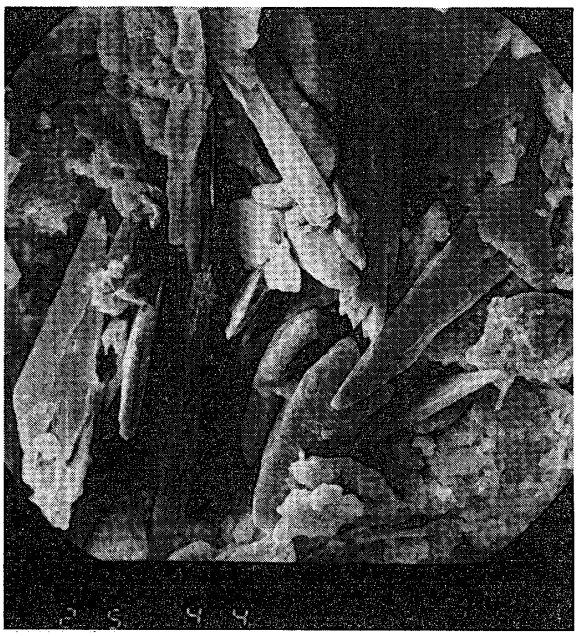

Fig. 8. Brushite. Sharp-ended crystals.

Fig. 9. Brushite. Tabular, foliated crystals with perfect cleavage.

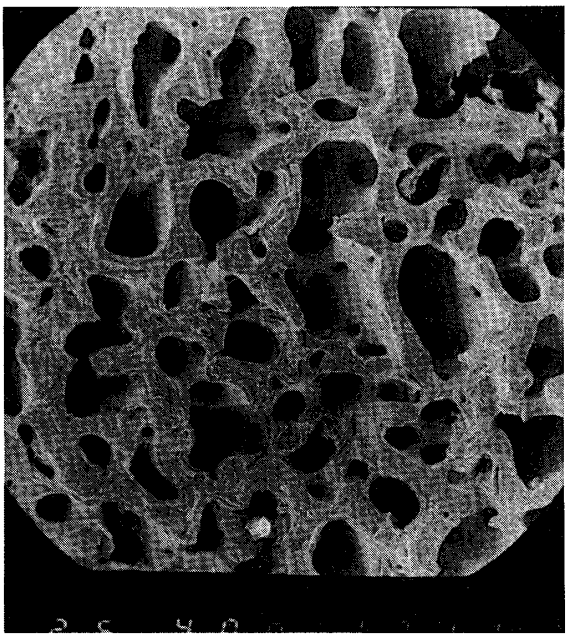

Fig. 10. Leucophosphite. Well-preserved structure of subfossil penguin bone built of pure leucophosphite.

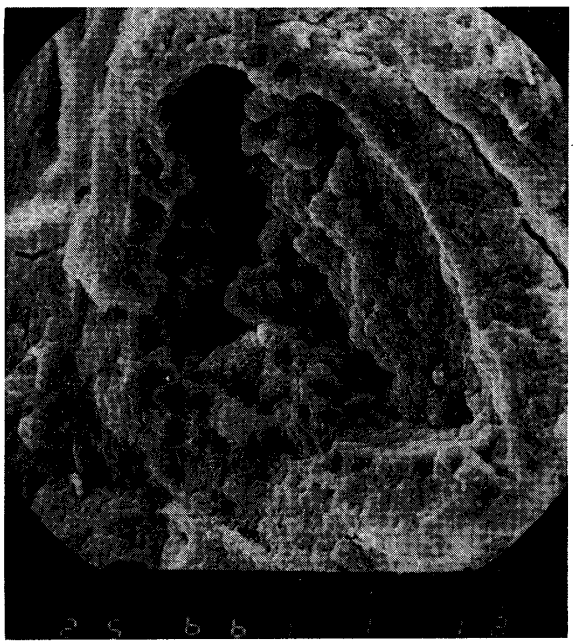

Fig. 11. Leucophosphite. Subfossil penguin bone. Microporous structure.

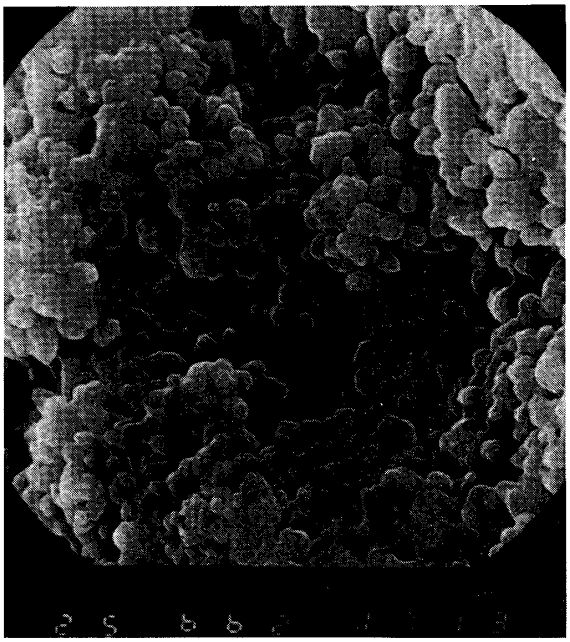

Fig. 12. Leucophosphite. Subfossil penguin bone. (?) Dissolved druse.

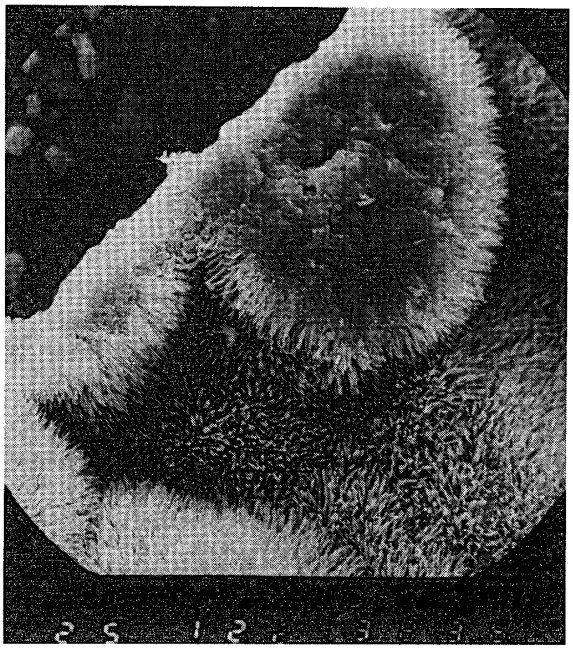

Fig. 13. Minyulite. Typical micro-druse of slender prisms.

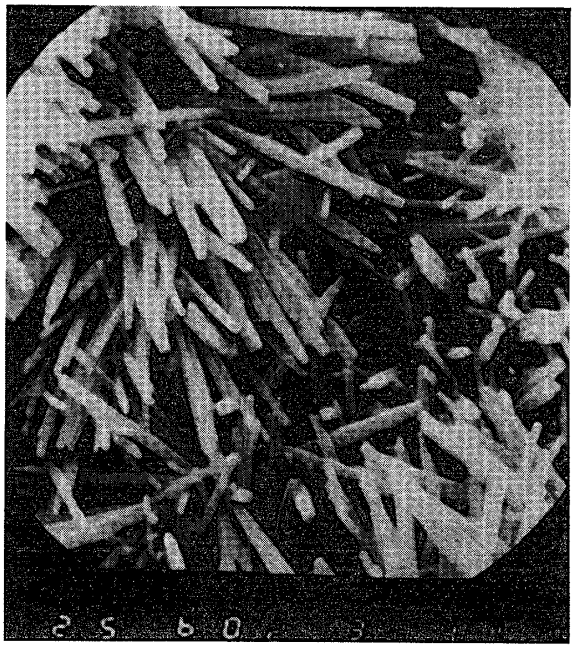

Fig. 14. Minyulite. Slender prisms.

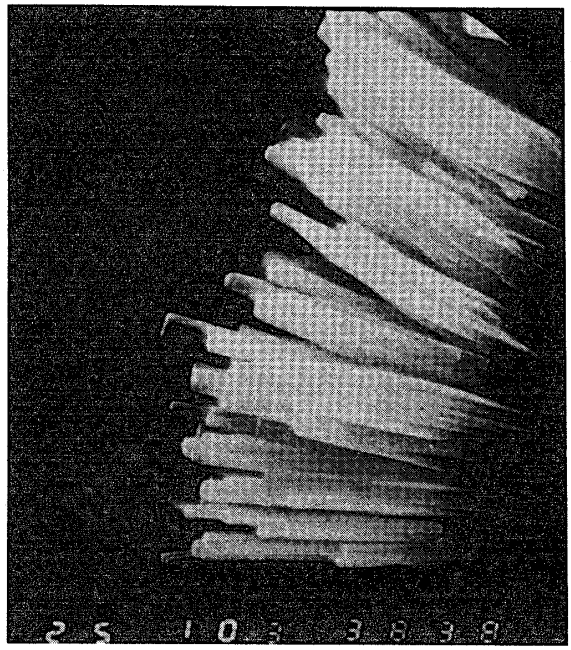

Fig. 15. Minyulite. Slender prisms with crystal system close to tetragonal.

Fig. 16. Minyulite. Druse of coarse prisms (rare case).

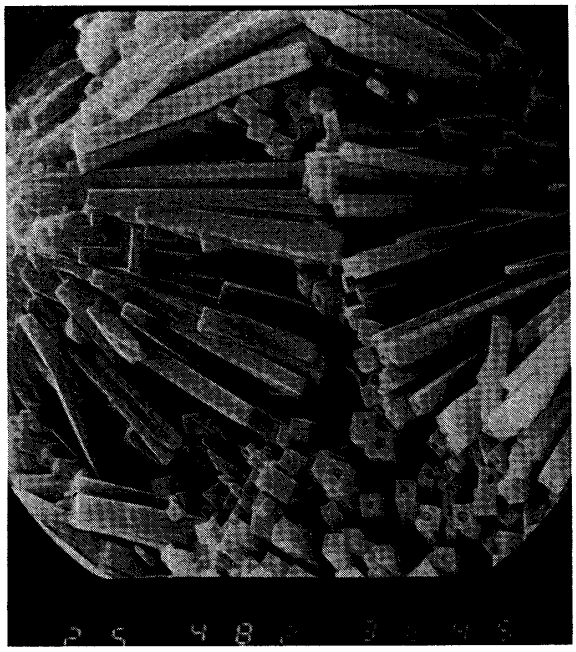

Fig. 17. Minyulite. Coarse prisms.

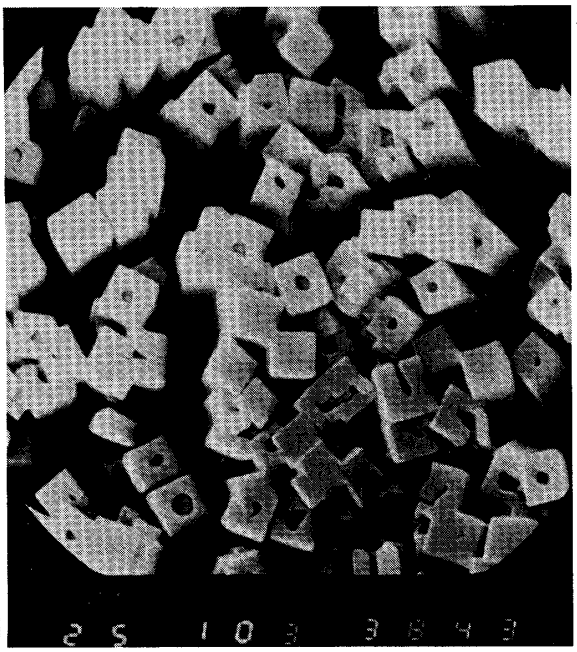

Fig. 18. Minyulite. Coarse prisms. Corrosion processes along Z axis weekness.

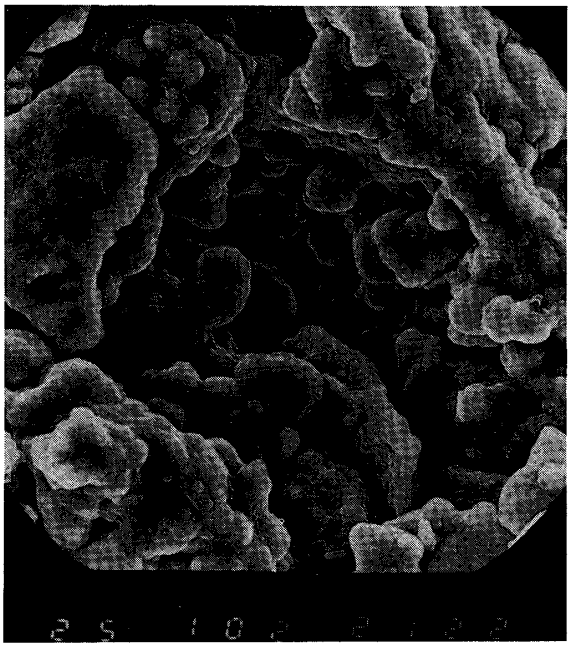

Fig. 19. Amorphous aluminium phosphate. Surface of the crust mineralization.

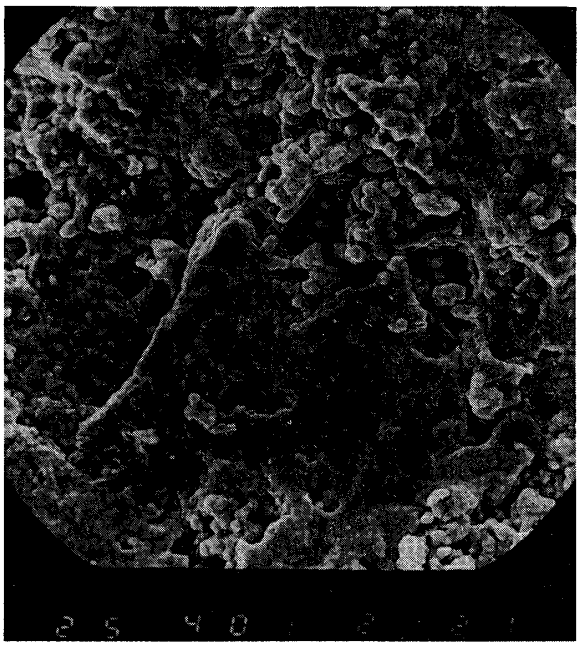

Fig. 20. Amorphous aluminium phosphate. Surface of the crust mineralization.

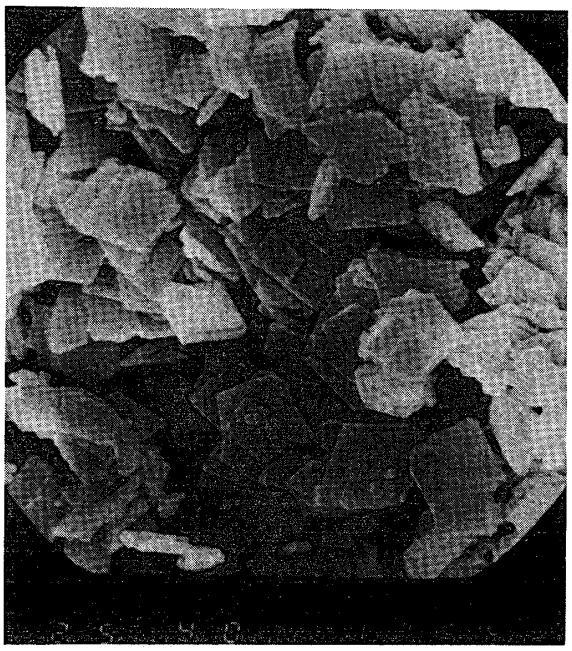

Fig. 21. Arctowskite. Rhombohedric plates.

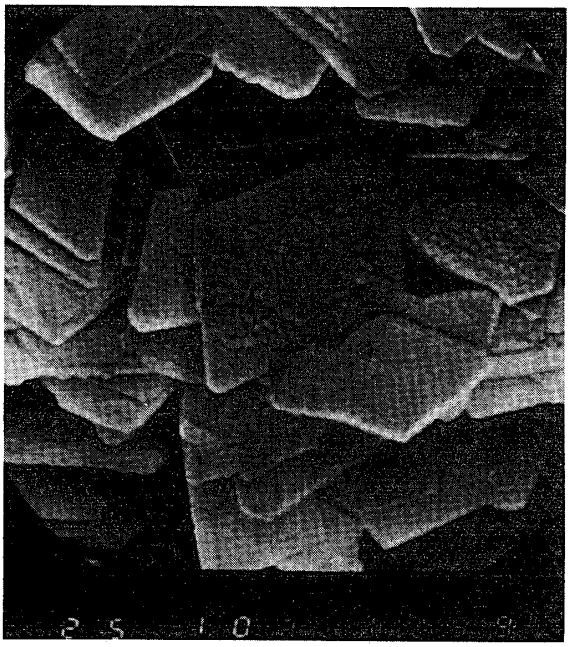

Fig. 22. Arctowskite. Twins of rhombohedric crystals.

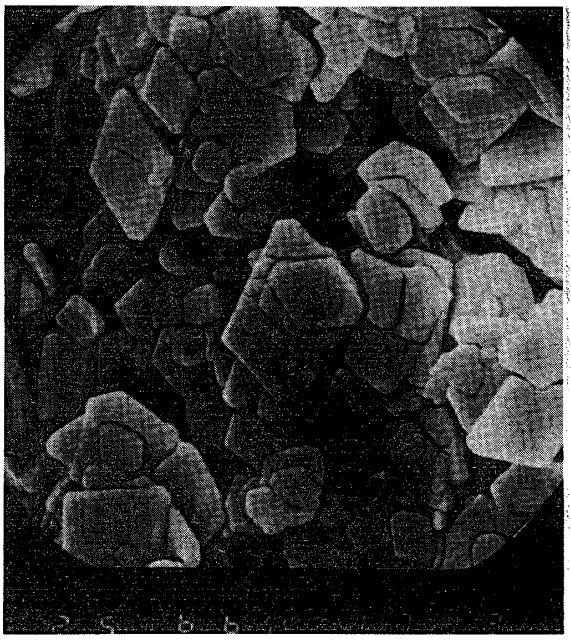

Fig. 23. Arctowskite. Plates disintegrating under the electron beam.

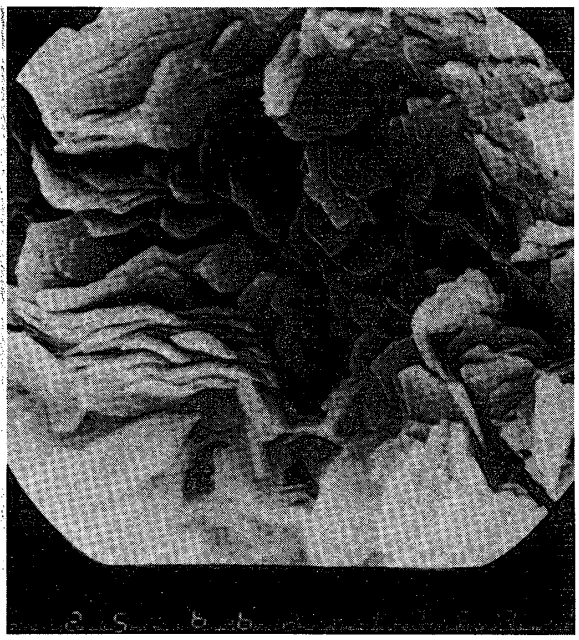

Fig. 25. Vashegyite-A. Rounded plates.

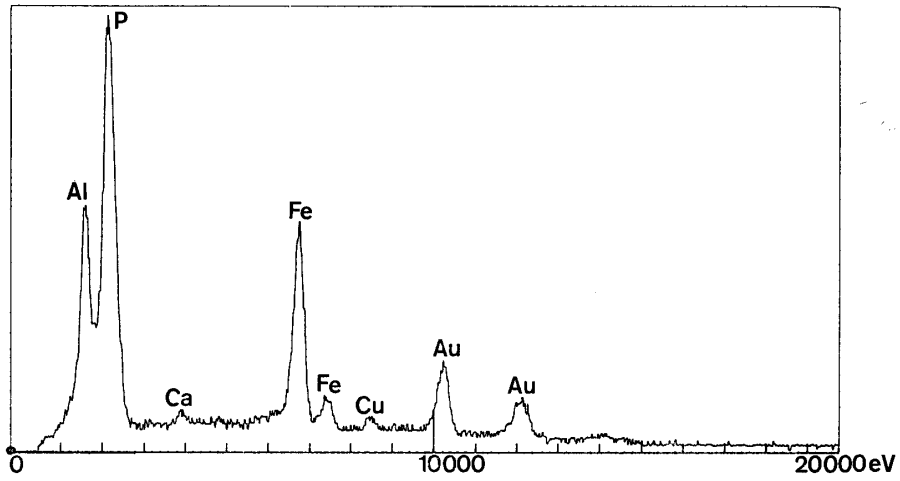

Fig. 24. Arctowskite. Energy dispersive X-ray pattern.

gyite-A as a result of feldspar phosphatization process is suggested. The chemical formula of this mineral seems to be simpler than in guide books: $(Al_{0.9}Fe_{0.1})(PO_4) *$ about $3.15H_2O$. In original vashegyite, the molar ratio of Al/P equals 4 : 3 (NRIAGU, 1984). However, the X-ray pattern of the sample is comparable with the typical one: 10.48/100, 8.71/5, 7.47/50, 7.07/30, 5.34/10, 4.02/10, 3.77/10, 3.67/10, 3.50/10, 3.29/10, 3.19/20, 2.92/35, 2.71/15, 2.52/10, 2.14/5. A long storing of the sample in the dry air of laboratory conditions did not cause any change in reflections.

Crystalline aluminium phosphate (vashegyite-B). This mineral was noted in one soil section only. It occurs in the permanently wet, and poorly aerated, lower part of the phosphatized rock zone in a relic ornithogenic soil near Arctowski Station, King George Island (outcrop, in TATUR, 1989). Vashegyite-B forms white, plastic material of clay grain size fraction dispersed mostly in soil and only sometimes concentrated in small lenses (sample 41 in TATUR, 1989). Subfossil penguin bones from this horizon (sample 4b2 in TATUR, 1989) are also built mainly of this mineral, but very poorly crystallized (Fig. 27). These bones are very soft and light colored. Vashegyite-B forms clay-like plates of irregular shapes (Figs. 28 and 29). Energy dispersive X-ray micro-analyses suggest a pure aluminium phosphate with traces of iron only (Fig. 30). In many points, however, traces of silica can be suggested from microanalyses (Fig. 31). Concentrations of fluorine (0.0258%) and sulphur (<0.01%) are low. Calculated chemical formula: $Al_{11}(OH, F)_3(PO_4)_{10} * 35H_2O$, gave a lower Al/P molar ratio than in the original vashegyite (NRIAGU, 1984), but a little higher than in vashegyite-A described above. The X-ray data: 9.80/100, 8.70/15, 7.44/50, 7.04/40, 5.40/10, 4.06/10, 3.77/10, 3.66/10, 3.49/10, 3.21/40, 2.92/60, 2.79/10, 2.69/10, 2.53/15, 2.13/5 are comparable with vashegyite described by MCCONNEL (1974). The sample stored in dry air of the laboratory of six months gave the same X-ray pattern.

Vivianite was found only in one place in the marginal zone of guano solutions influence. It formed a few aggregates of crystals in clay underlying peat at a depth of about one meter (TATUR and BARCZUK, 1984).

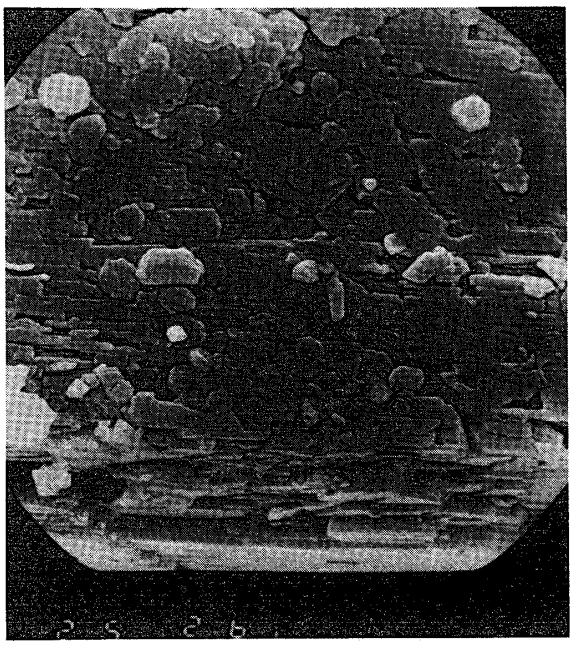

Fig. 26. Vashegyite-A. (?) Formation of this mineral (rounded plates) as a result of feldspar phosphatization (wall).

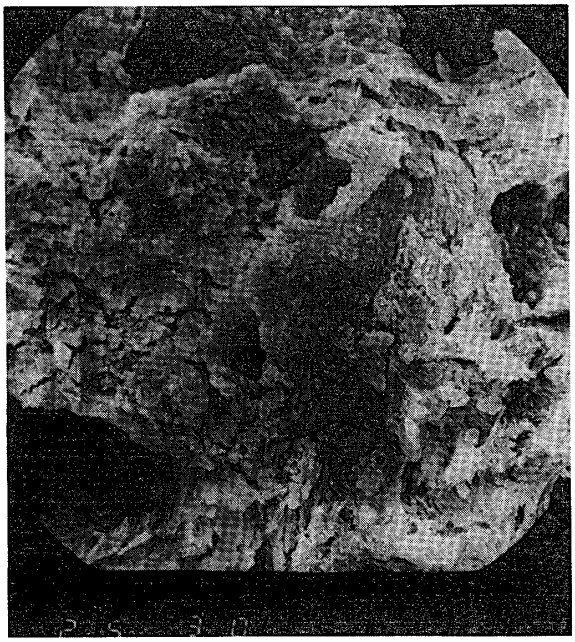

Fig. 27. Vashegyite-B. Subfossil penguin bone. Poorly crystallized mineral.

Fig. 28. Vashegyite-B. Clay-like habit of well-defined crystal plates.

Fig. 29. Vashegyite-B. Individual plates.

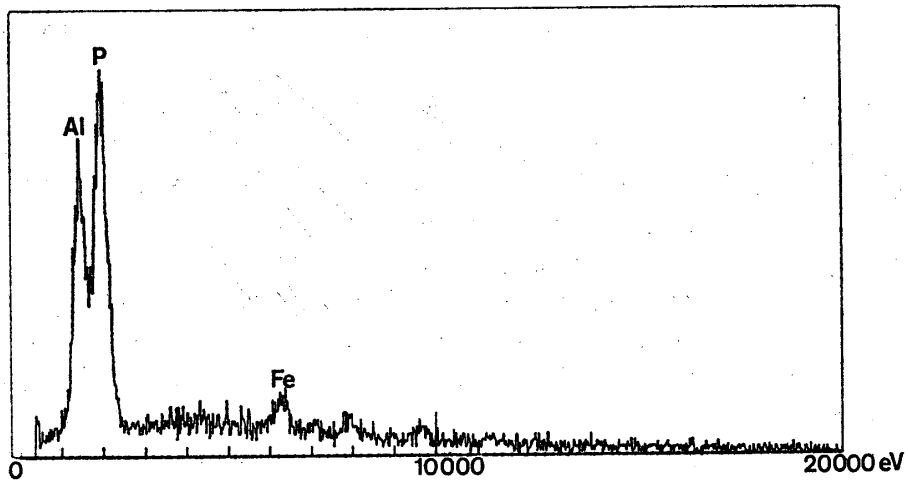

Fig. 30. Vashegyite-B. Energy dispersive X-ray pattern.

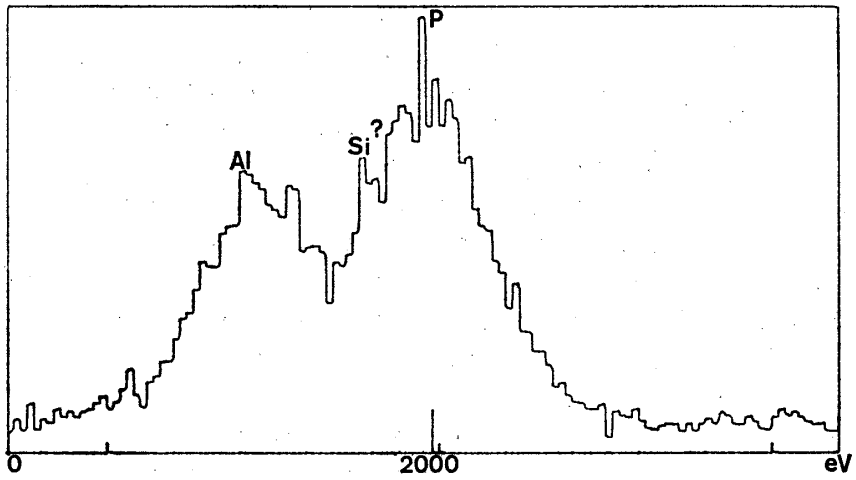

Fig. 31. Vashegyite-B. Detaits of energy dispersive X-ray pattern.

4. Conclusion

Phosphate mineralization in soils resulted from the huge concentration of birds is commonly known on the sea coast adjacent to highly productive sea regions. Such areas also occur on the dry, southeast coast of South America and extend southward to wet archipelagos of the maritime Antarctic and further to the coastal zone of the Antarctic Peninsula. On the other hand, on the Antarctic Continent, lack of water due to low temperatures precludes phosphatization of the parent rock, and only accumulation of humus-like guano is observed on the area of penguin rookeries.

Processes of phosphatic mineralization in coastal soils of the maritime Antarctic Zone seem to be specific of this region. Snow and rain precipitations in this area are quite high as compared with those on the coast of Patagonia. Nevertheless, strong wind and daily freezing-melting cycle during the summer season account for superconcentrations of guano solutions washing the rookery, and thus precipitation of phosphates in the ornithogenic soil is possible. Because of the periodic abundance of water, phos-

phatized rock zone can be well developed but guano layer relatively quickly undergoes dissolution.

In the maritime Antarctic, several specific mineralogical features are also coming from the food of penguins. Penguins feed on krill, which contains a lot of fluorine and trace metals (Sr, Zn, Cu). All of them concentrate in guano, and fluorine is a very important phosphate-forming element in guano as well as in the phosphatized rock zone.

The present analysis of the occurrence of phosphates in ornithogenic soils in the maritime Antarctic Zone led to an enlargement of the conclusions already published step by step in several papers (TATUR and BARCZUK, 1984, 1985; MYRCHA *et al.*, 1985; TATUR, 1987, 1989). Vertical distribution of phosphates in soil profile depends above all on the soil pH varying with depth. Phosphates of guano layer are stable at alkaline and neutral reactions, phosphates of the upper part of phosphatized rock zone occur at neutral and slightly acid reactions but of the lower part at permanently acid one.

However, this simple ralationship is modified by several other soil properties. The excess of magnesium ions coming from the sea water, besides phosphorus and ammonia ions of ornithogenic origin, results in struvite precipitation. The excess of fluorine (of krill origin) enhances the formation of fluorine-bearing minerals: fluorapatite, sometimes even (?) fluorite instead of hydroxyapatite in the guano layer and amorphous aluminium phosphates bearing high fluorine content, or minyulite in the phosphatized rock zone (KAMPF, 1977). Mobility of iron in organic rich soil accounts for leucophosphite formation under the guano layer, whereas the leaching of entire iron together with the excess of fluorine can enhance minyulite formation. Taranakite is formed not only from the most acid but also from the most diluted solutions, usually under the level of ground water. Washing of all aluminium-iron phosphates bearing potassium and ammonia ions by poorly mineralized rain and melting water incongruently dissolves them with creation of amorphous aluminium phosphates.

Important mineralogical changes took place during weathering process in the ornithogenic soils of the areas abandoned by penguins. Struvite and urates disappear at once. Gradual mineralization of organic matter causes the concentration of apatite in a relic guano layer. Apatite can also be totaly dissolved during resting for a long time on the soil surface. From the complex crust mineralization on the surface of the rock and stones, single minerals can be left as a result of selective dissolution during weathering. From the paragenesis of struvite+apatite only apatite remains, but from the paragenesis apatite+amorphous aluminium phosphate the second one is more durable.

The phosphates of the phosphatized rock zone are in general much more abundant than those of guano in relic ornithogenic soils. Only minyulite seems to be unstable in weathering processes. Leucophosphite, taranakite and aluminium phosphates are common. It may be suggested that they could also be formed due to guano dissolution and reaction of guano leachates with silicates after penguins left the nesting places.

Among all ornithogenic phosphates, crystalline aluminium phosphates (vashegyite, arctowskite) were found only in relic ornithogenic soils. This observation suggests that aging of phosphate deposits supports their formation.

Phosphate mineralization in soils has been developed in complex processes of guano mineralization and phosphatization of silicate weathered loams derived from volcanic rock. The guano minerals (urates, apatite, struvite, fluorite) were formed directly as an

effect of drying of liquid excretion (urates), or due to the evaporation of solutions washing mineralized excreta and guano. Much more complicated is the genesis of phosphates created in phosphatization processes of underlying rock. Most of aluminium and iron phosphates bearing potassium and ammonia ions precipitate also from supersaturated soil solution. It means that not only phosphorus and ammonia (gauno elements) but also aluminium, iron and potassium (rock elements) can be carried on by the soil water over a long distance before their precipitation.

In the phosphatized rock zone many phosphates are also formed by the effect of metasomatic processes. Usually solutions carrying phosphorus infiltrate into the weathered rock and form variable phosphatic pseudomorphs in the place of silicate minerals. Very common are also hard crusts of amorphous aluminium phosphates and sometimes also minyulite around phosphatized clastic grains of volcanic rocks. Aluminium released from altered grains precipitates immediately phosphate ions over them.

In the case of vashegyite-B the renewed idea can be suggested about isomorphous replacement of silica tetrahedra by phosphoric acid tetrahedra in the crystal structure of clay minerals during phosphatization process (McConnell, 1974). The shape of phosphates and (?) X-ray pattern seems to be hereditary after phosphatized crystals of clay minerals, what seems to be also supported by the microanalyses (Fig. 31). In such a case the course of this reaction might be considered as the phosphatization process on the elemental crystallochemical level. This hypothesis has been inferred for a long time by many scientists, but still is a controversial issue (Flicoteaux and Lucas, 1984).

Mineral transformations in the phosphatized rock zone can be sometimes very surprising. Subfossil bones (older than 5 thousand years) have been altered as a result of decalcification at acid soil reaction into pure leucophosphite (mixed conditions of aeration), or into poorly crystallized vashegyite-B (permanently anoxic conditions), while the microstructure of the bones was left unchanged. In this case cations have been exchanged and finally formed "*in situ*" new crystalline phosphates. During these processes phosphorus remained in the bones.

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